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14. ABSTRACT

Isothermal Frontal Polymerization (IFP) is a polymerization method that propagates directionally as opposed to homogeneous polymerization. The propagation distances of Poly(Methyl Methacrylate)/Methyl Methacrylate systems can be increased by increasing the parameters of initiator decomposition rate, initiator concentration, and temperature and/or by adding a polymeric inhibitor to the bulk solution. IFP does not depend on the size of the polymeric seed, but a critical seed molecular weight must be maintained for maximum propagation. The current method of front detection is invasive and inadequate giving quantitatively irreproducible results, and thus, a new detection method is required.

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Final Technical Report for AFOSR grant <u>F49620-97-1-0378</u>
Preparation of Organic Dye Gradients for Optical Limiters

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Introduction:

Isothermal Frontal Polymerization (IFP), or Interfacial Gel Polymerization, is a process of polymerizing monomer in a progressive direction and can incorporate secondary substances to produce gradient materials. Typically monomer and thermal initiator are placed on a polymeric seed (monomer that has been bulk polymerized). The seed and monomer solution diffuse into one another creating a region of high viscosity. The diffusion creates a gradient of concentrations, but there are considered to be three regions: The bulk region, monomer and initiator; the viscous region, monomer, initiator, and dissolved polymer; and the polymer seed, undissolved polymer. The thermal initiator is a radical initiator, and radical polymerization occurs both in the bulk region and in the viscous region. Polymerization occurs faster in the viscous region due to the Trommsdorff, or gel, effect. The newly formed polymer and the bulk region diffuse into one another continuing the process, and thus progressive polymerization occurs, which is termed frontal polymerization, Figure 1.
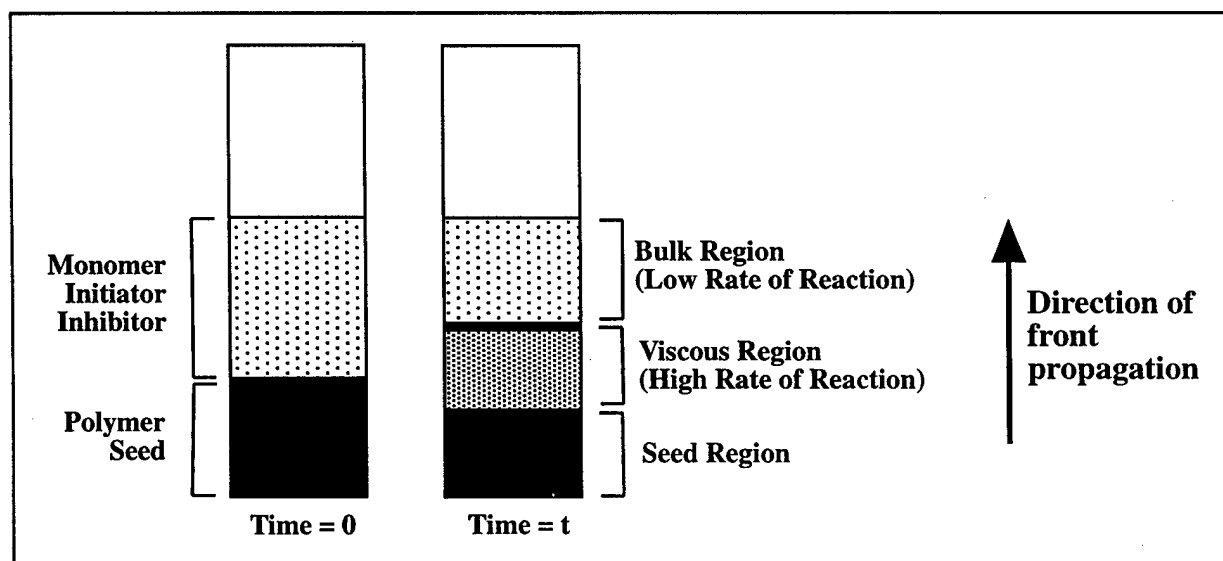
Figure 1: Schematic of IFP

While this process is used to produce gradient materials, such as laser-hardened materials, optical limiters, and Gradient Refractive INdex Materials (GRINs), there has not been much published on how the parameters affect the process. The parameters of initiator decomposition rate, initiator concentration, experimental temperature, inhibitor, seed molecular weight, and seed dissolution time of the polymer/monomer system of poly(methyl methacrylate)/methyl methacrylate (PMMA/MMA) have been examined. Systems varying the first four parameters have been compared to mathematical simulations.

Experimental Procedure:

The chemicals used are listed in Table 1 with their names, abbreviations, percentages of purity, and sources. MMA was purified with a mono-methyl ether hydroquinone inhibitor-removal column. The water was removed by adding calcium hydride (CaH_2) and filtering with a 0.4 μm filter. The initiator 2,2'azobisisobutyronitrile (AIBN) was recrystallized in methanol and filtered. It was then washed with cold methanol and then cold water and was repeated three times. All other chemicals were used as purchased.

Table 1: Chemicals Used: Abbreviations, Percentages of Purity, and Sources

Chemical	Abbreviation	% Purity	Source
9-anthracenylmethyl methacrylate	PolyFluor 407		Polysciences, Inc.
2,2'azobisisobutyronitrile	AIBN	98	Aldrich
calcium hydride	CaH_2	90-95 (-40 mesh)	Aldrich
2,3-dimethyl-2,3-diphenyl butane	Perkadox 30		AKZO Chemicals
lauroyl peroxide	LPO	97	Aldrich
methyl methacrylate	MMA	99	Aldrich
3,3',4',5,7-pentahydroxyglavone	Quercetin		Sigma
poly(4-vinylphenol)	P4VP		Aldrich
1,1-di-tert-butylperoxy-3,3,5-trimethyl cyclohexane	Lupersol 231		ATO Chemicals
2,2,6,6'-tetramethyl-1-piperidinyloxy	TEMPO	98	Aldrich

The polymeric seeds were manufactured as follows: Two milliliters of 2.0 mM AIBN/MMA solution were placed in a 13.5 mm inner diameter (15 mm outer diameter) screw-top test tube (Fisher # 60826-188), capped with argon, and placed in a 70°C thermostated water bath for 51 hours. The seeds were then placed in a 100°C oven for 24 hours to ensure that no initiator remained. Some seeds were made with an additional 0.1% 9-methyl anthracenyl methacrylate, which was used as a fluorescent marker.

To run the front, approximately 7.0 mL of 2.0 mM initiator/MMA solution was placed in the test tube onto the seed, the tube was placed in the thermostated water bath at the experimental temperature, and the front was allowed to propagate. The propagation of the front was determined by taking the tube out of the water bath and tilting it slightly to see the solid-liquid interface, which was considered to be the position of the front, Figure 2.
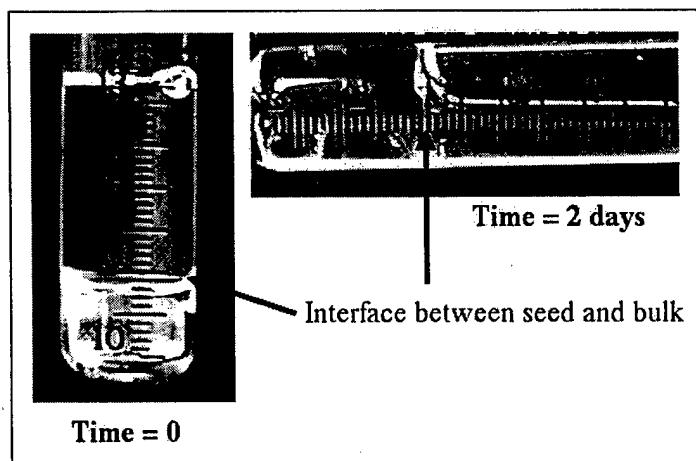
Figure 2: Determination of Front Propagation

A plot of the front position with respect to time showed the behavior of the front (Figure 3, Data A). In order to have a true measurement of the front, the amount of seed dissolution had to be removed from the amount of propagation: There was an induction period for the bulk region and seed region to diffuse into one another creating the viscous region before the front could begin to propagate. This initial dissolution, as well as continued dissolution, was shown by the addition of Polyfluor 407 to the seed solution where it was chemically incorporated into the polymer seed. After a front progressed, the sample was sliced into segments, which were examined under ultraviolet light, and all segments of the polymerized front contained the fluorescent compound. The seed dissolution was measured by running a control front of 2.0 mM 2,2,6,6'-tetramethyl-1-piperidinyloxy (TEMPO)/MMA solution (Figure 3, Data B). (TEMPO was a free-radical scavenger used to ensure that no polymerization occurred in the sample.) In order to calculate the amount of front propagation, the data during the time of seed dissolution were truncated, and the data for the seed dissolution were subtracted (Figure 3, Data C).

Results and Discussion:

Typical experimental values in the Pojman lab and literature values for front propagation were under one centimeter. Propagation was stopped by homogeneous polymerization of the bulk solution. In order to increase the length of propagation, an inhibitor was added to the bulk solution to slow this homogeneous polymerization of the bulk solution. Three inhibitors were used: TEMPO, poly-4-vinyl-phenol (P4VP), and 3,3',4',5,7-pentahydroxyglavone (Quercetin). Table 2 lists averages of these fronts with the initiator lauroyl peroxide (LPO) at 70°C.
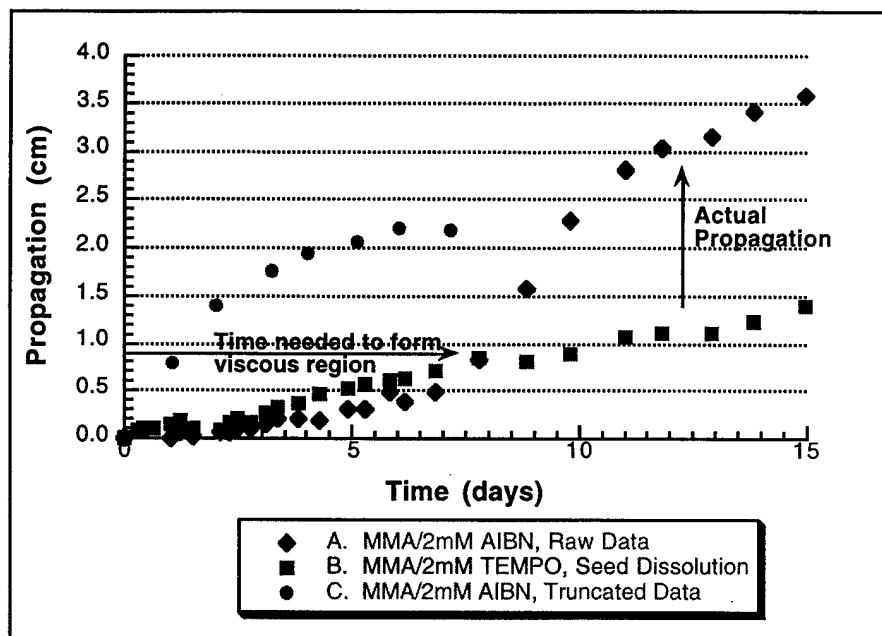
Figure 3: Subtraction of Seed Dissolution

Table 2: Measure Front Propagation* for Varied Inhibitors for Systems of 2.0 mM LPO/MMA at 70-C

Inhibitor	Length of Propagation (cm)	Time of Propagation (hours)
TEMPO	2.2	270
P4VP	3.3	170
Quercetin	1.2	45

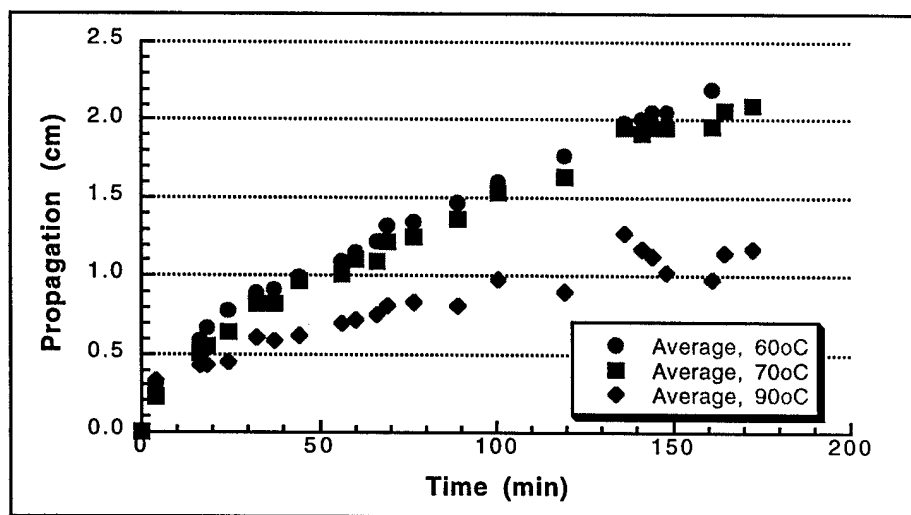(*This data did not have seed dissolution subtracted from it.)

From these data and other data, it was concluded that the order of strongest to least inhibitor for the IFP system of LPO/MMA was TEMPO, P4VP, and Quercetin. Systems containing TEMPO did not propagate as far as systems with P4VP, but homogeneous polymerization of the bulk solution occurred much later. Thus, TEMPO was more efficient at preventing polymerization. TEMPO could not be used in further studies to extend the life of the front, because it diffused into the viscous region preventing frontal polymerization. To determine the maximum length of propagation with the inhibitor P4VP, fronts were run with four separate initiators: AIBN, LPO, 2,3-dimethyl-2,3-diphenyl butane (Perkadox 30), and 1,1-di-tert-butylperoxy-3,3,5-trimethyl cyclohexane (Lupersol 231). The average propagation lengths are shown in Table 3. For the polymeric phenolic inhibitor P4VP, the greatest length of propagation was achieved with the initiator LPO. The inhibiting effects of P4VP were from strongest to least: LPO, Perkadox 30, Lupersol 231, and AIBN.

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Table 3: Measure of Front Propagation* for Varied Initiator Decomposition Rates for Systems of 2mM Equivalent P4VP/MMA at 70-C

Initiator	Length of Propagation (cm)	Time of Propagation (hours)
AIBN	0.4	5
LPO	3.5	170
Perkadox 30	1.3	80
Lupersol 231	0.9	30

(*This data did not have seed dissolution subtracted from it.)

     The effect of seed molecular weight was tested. To vary the molecular weight of the seeds, they were polymerized at different temperatures, 60°C, 70°C, and 90°C, with higher temperatures producing lower molecular weights. The percentage conversion was also altered by polymerizing seeds at each of the temperatures for periods of 12, 24, 36, and 48 hours, where the lower time gives a lower percentage conversion. (Percentage conversions were determined by differential scanning calorimetry, were 97% for 12 hour seeds, and were increasing for longer polymerization times.) Fronts were run with a bulk solution of 2.0 mM Perkadox 30/2.0 mM equivalent P4VP/MMA. The lengths of propagation of the fronts at 60 and 70°C were about 2.0 cm in 7 days and for 90°C were about 1.5 cm in 7 days. Thus, when fronts were run below a critical seed molecular weight, there was a decrease in the amount of propagation, Figure 4.

Figure 4: Fronts* of 2.0 mM Perkadox 30/2.0 mM Equivalent P4VP/MMA Using Different Seed Molecular Weights
(*This data did not have seed dissolution subtracted from it.)

To study the propagation more efficiently, the IFP system was simplified to a bulk solution of initiator/MMA, and the temperature was lowered. The parameters of initiator decomposition rate, initiator concentration, and experimental temperature were varied and compared to mathematical simulations from Cynthia Spade and Vladimir Volpert of Northwestern University, Figures 5-7.
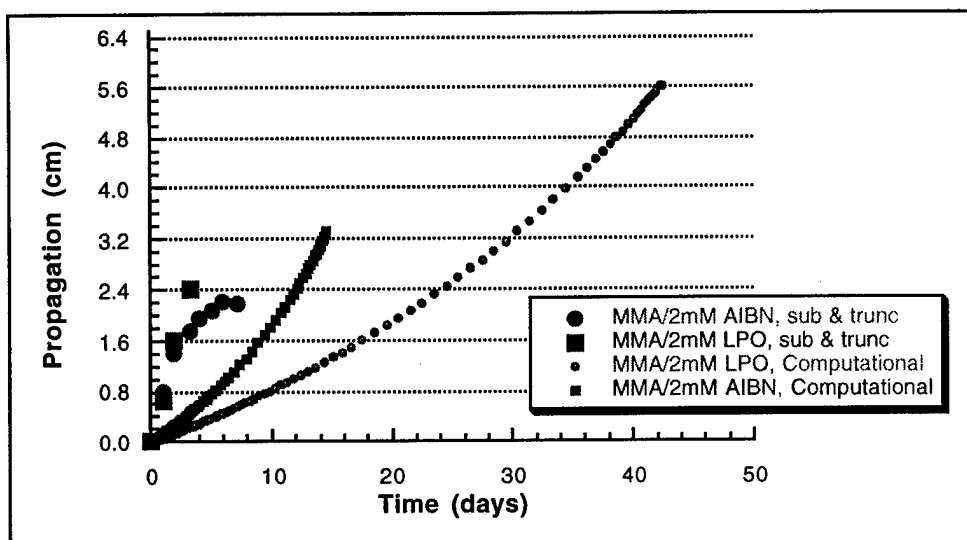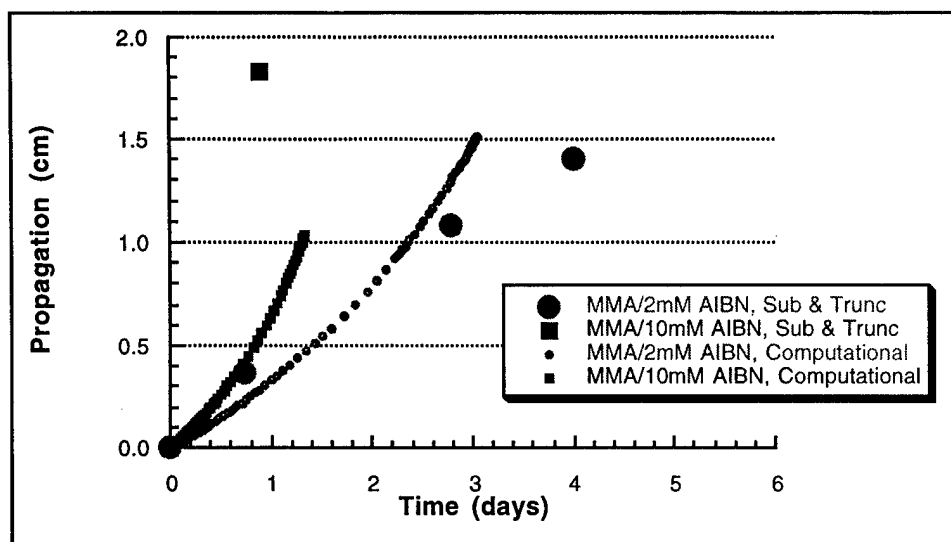

Figure 5: Computational and Experimental Results[*] Where Initiator Decomposition Rate Was Varied
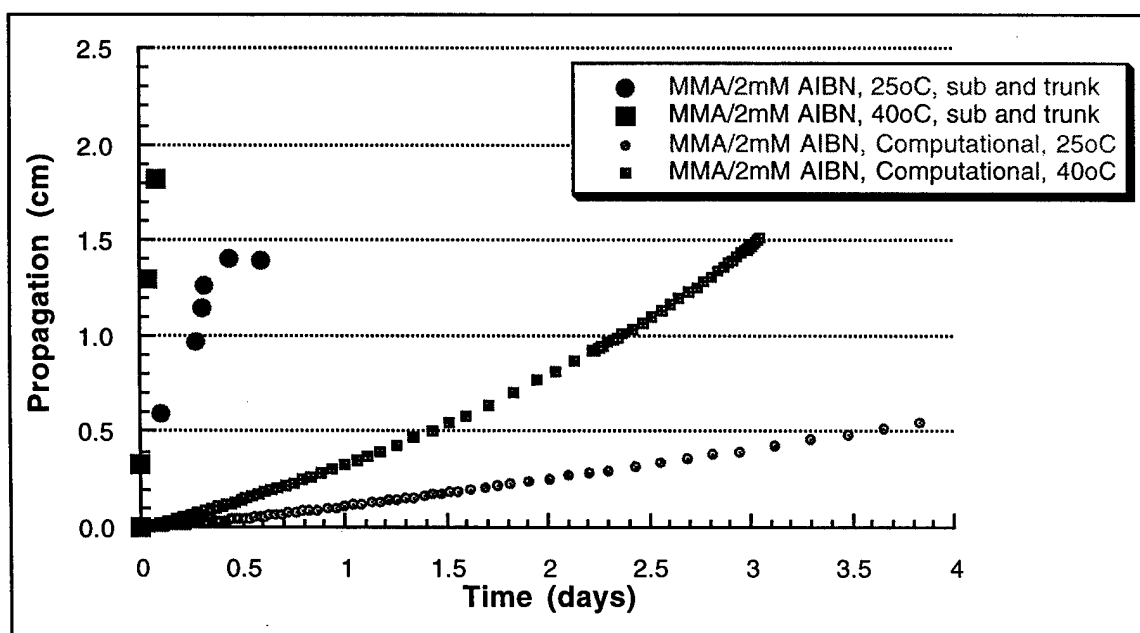([*]Data were calculated by the method outlined in Figure 3.)

Increasing any parameter caused an increase in the rate of propagation but a decrease in the length of propagation due to the bulk solution homogeneously polymerizing more quickly. This model did not include seed dissolution at any time during the front process. The experimental system included dissolution and an undetermined amount of inhibition due to oxygen. The results of their models qualitatively agreed with the experimental trend of increased rate of polymerization with a decrease in life of the front due to an increase in parameter. The experimental factors of seed dissolution and inhibition possibly contributed to the differences between the mathematical simulations and experimental data, as well as the nature of the mass diffusion, the conditions at the boundaries of the model, the values of the kinetic parameters of the model, and the profile of the termination rate constant due to the gel effect.

Figure 6: Computational and Experimental Results[*] Where Initiator Concentration Was Varied

([*]Data were calculated by the method outlined in Figure 3.)

**Figure 7:** Computational and Experimental Results[*] Where Temperature Was Varied

([*]Data were calculated by the method outlined in Figure 3.)

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To reduce the seed dissolution time of the experimental fronts, seeds of 2.0 mL to 0.25 mL (1.0 to 0.2 cm in height) were made. Their dissolution was measured in a 2.0 mM TEMPO/MMA solution. The 0.5 mL seeds did not support a front, and fronts of 0.75 mL exhibited similar behavior to 2.0 mL seeds, Figure 8. Thus, only the top layer of seed participated in the IFP process. To preswell seeds, they were ground into powder and mixed with 2.0 mM AIBN/MMA to make solutions of 20.0 to 40.0 volume/weight percentage. Seven milliliters of 2.0 mM AIBN/MMA solution were placed on top and allowed to propagate at 40°C, Figure 9. These solutions took longer to reach the critical viscosity necessary for frontal polymerization.
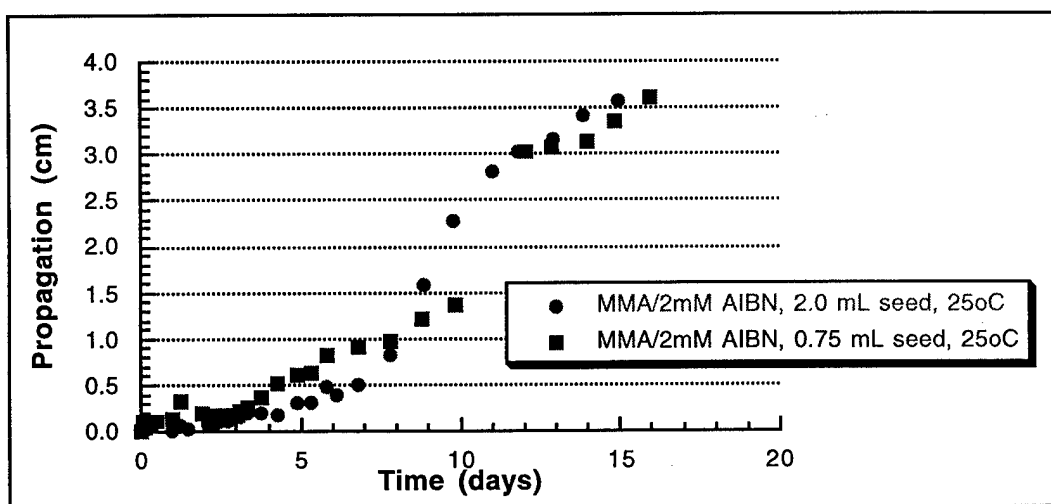
Figure 8: Propagation* of 2.0 mM AIBN/MMA Solutions Using 2.0 and 0.75 mL Seeds
(*This data did not have seed dissolution subtracted from it.)

Samples were degassed under vacuum using a freeze-thaw degas method to remove the inhibitor oxygen. Propagation of these fronts was similar to samples not degassed, and gas chromatography showed that five percentage of oxygen remained in the degassed samples. Thus, this method of freeze-thaw degassing was not efficient at removing suitable quantities of the inhibitor oxygen.
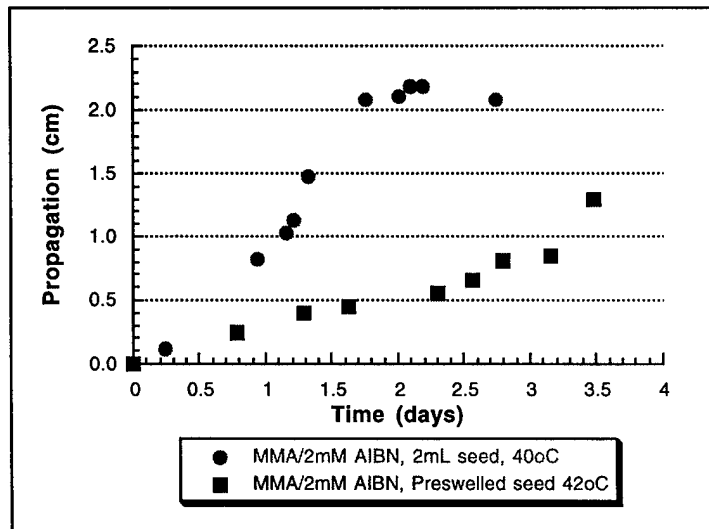
Figure 9: Propagation[*] of 2.0 mM AIBN/MMA Solutions with Regular and Preswelled Seeds

([*]This data did not have seed dissolution subtracted from it.)

Conclusions:

To maximize the propagation of a PMMA/MMA front, any of the parameters of initiator decomposition rate, initiator concentration, and experimental temperature were increased, a polymeric inhibitor was added to the bulk solution, and a critical seed molecular weight was used. It was not efficient to remove the inhibitor oxygen from the system, to reduce the amount of seed used, nor to preswell the seed. Because of the monitoring procedure used in IFP experiments for this work, all the work in this report was qualitative with no quantitative reproducibility. Thus, a non-invasive monitoring technique is needed to determine precise propagation lengths and times, rather than trends.